TC1 – Grundlagen der Theoretischen Chemie

Irene Burghardt (burghardt@chemie.uni-frankfurt.de)

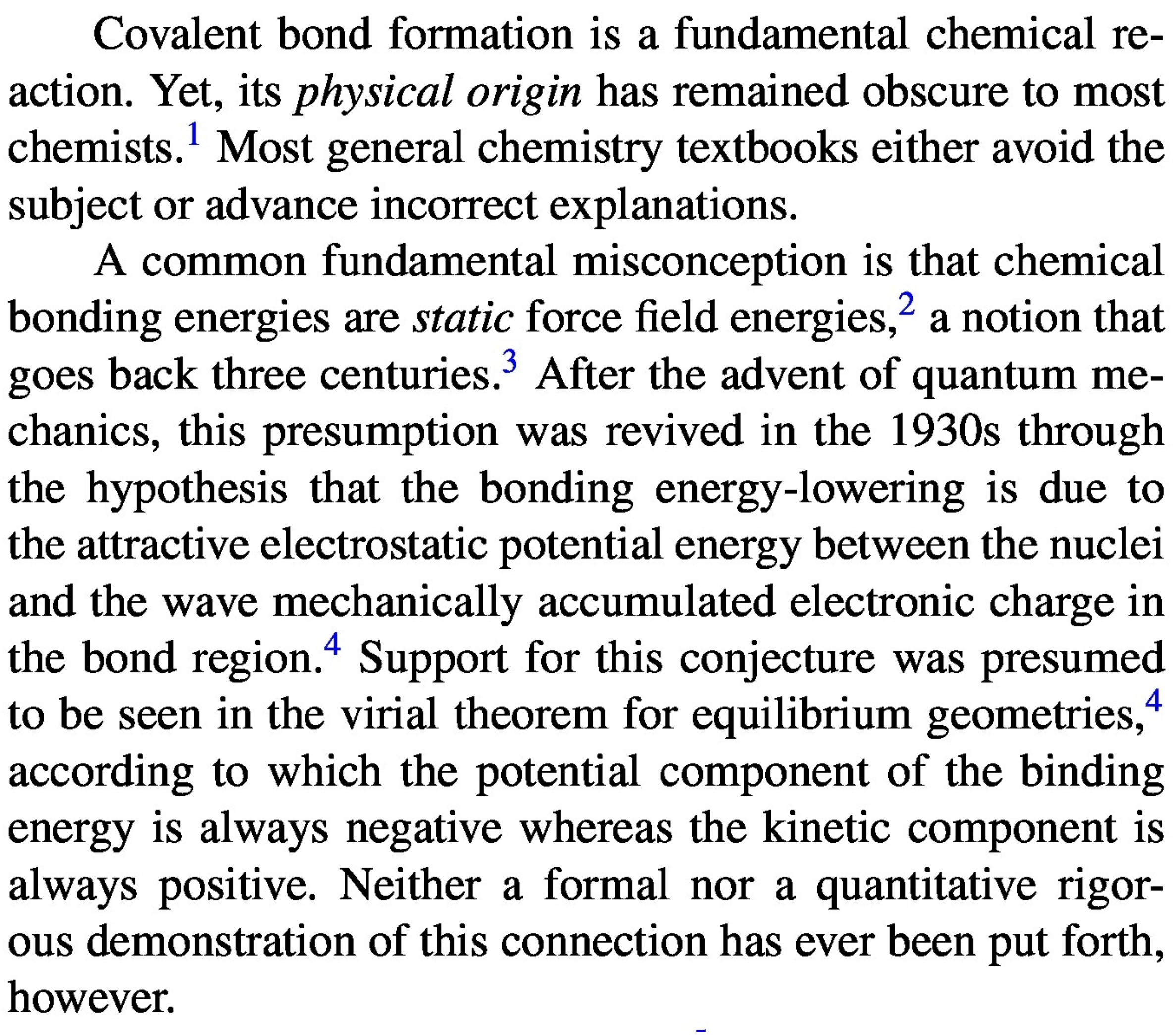
Praktikumsbetreuung:

Konstantin Falahati (k.falahati@yahoo.com)
Jan von Cosel (jvcosel@theochem.uni-frankfurt.de)
Robert Binder (rbinder@theochem.uni-frankfurt.de)
Tianji Ma (beiai@hotmail.de)

Vorlesung: Di 10h-12h, Fr 9h-10h
Übungen: Fr 10h-11h

Web site: http://www.theochem.uni-frankfurt.de/TC1

Natur der kovalenten Bindung



Covalent bond formation is a fundamental chemical reaction. Yet, its *physical origin* has remained obscure to most chemists.[1] Most general chemistry textbooks either avoid the subject or advance incorrect explanations.

A common fundamental misconception is that chemical bonding energies are *static* force field energies,[2] a notion that goes back three centuries.[3] After the advent of quantum mechanics, this presumption was revived in the 1930s through the hypothesis that the bonding energy-lowering is due to the attractive electrostatic potential energy between the nuclei and the wave mechanically accumulated electronic charge in the bond region.[4] Support for this conjecture was presumed to be seen in the virial theorem for equilibrium geometries,[4] according to which the potential component of the binding energy is always negative whereas the kinetic component is always positive. Neither a formal nor a quantitative rigorous demonstration of this connection has ever been put forth, however.

J. Chem. Phys. 140, 204104 (2014)

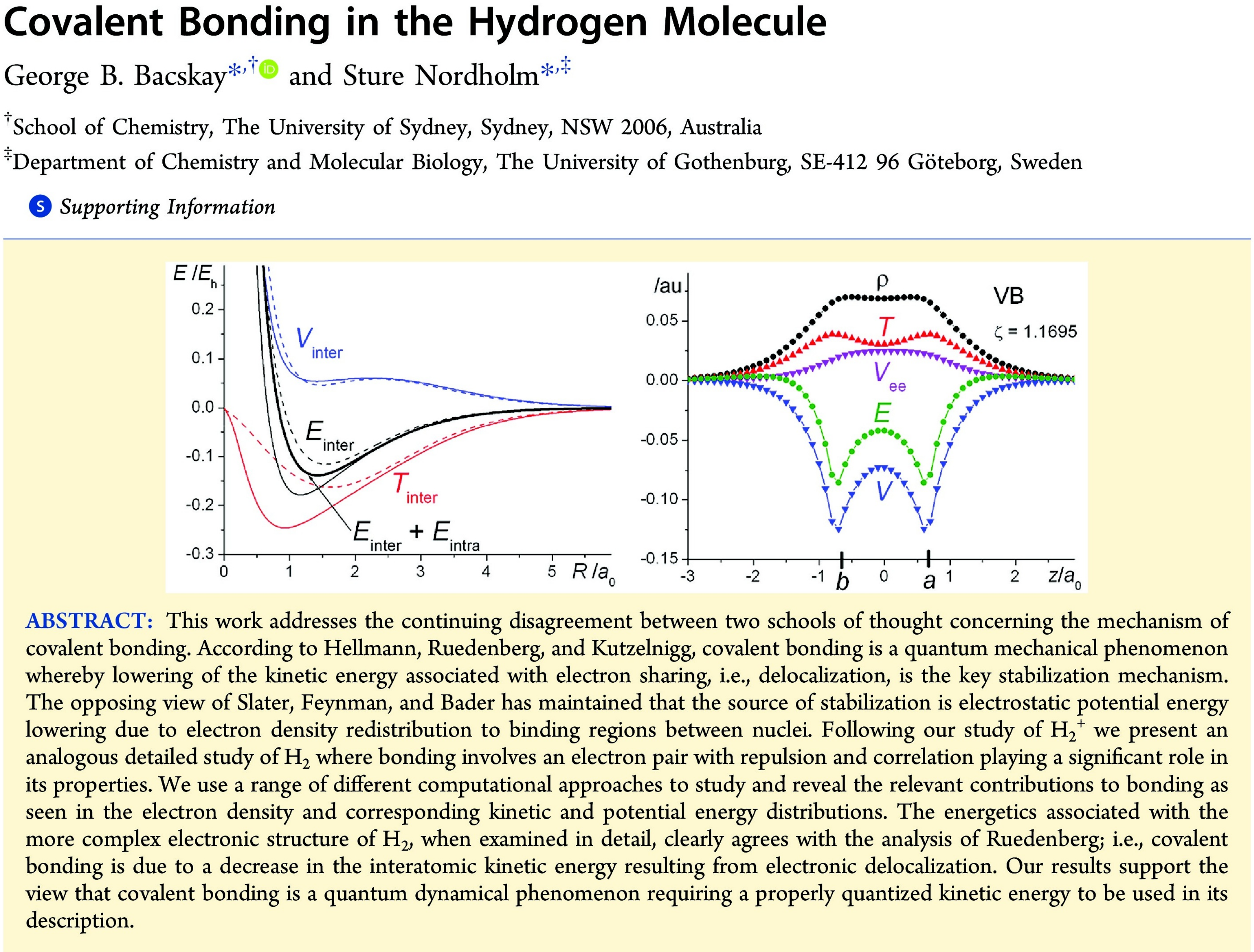
Natur der kovalenten Bindung

Zwei Hypothesen:

1. **Slater, Feynman, Bader: Delokalisierung der Elektronendichte in der Bindungsregion führt zur elektrostatischen Stabilisierung**

2. **Hellmann, Rüdenberg, Kutzelnigg: Delokalisierung der Elektronendichte in der Bindungsregion führt zur Absenkung der kinetischen Energie und der damit einhergehenden Stabilisierung**

Neuere quantitative Studien zeigen eindeutig, dass (2) korrekt ist!



Covalent Bonding in the Hydrogen Molecule

George B. Bacskay*,† and Sture Nordholm*,‡

†School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia
‡Department of Chemistry and Molecular Biology, The University of Gothenburg, SE-412 96 Göteborg, Sweden

S *Supporting Information*

ABSTRACT: This work addresses the continuing disagreement between two schools of thought concerning the mechanism of covalent bonding. According to Hellmann, Ruedenberg, and Kutzelnigg, covalent bonding is a quantum mechanical phenomenon whereby lowering of the kinetic energy associated with electron sharing, i.e., delocalization, is the key stabilization mechanism. The opposing view of Slater, Feynman, and Bader has maintained that the source of stabilization is electrostatic potential energy lowering due to electron density redistribution to binding regions between nuclei. Following our study of H_2^+ we present an analogous detailed study of H_2 where bonding involves an electron pair with repulsion and correlation playing a significant role in its properties. We use a range of different computational approaches to study and reveal the relevant contributions to bonding as seen in the electron density and corresponding kinetic and potential energy distributions. The energetics associated with the more complex electronic structure of H_2, when examined in detail, clearly agrees with the analysis of Ruedenberg; i.e., covalent bonding is due to a decrease in the interatomic kinetic energy resulting from electronic delocalization. Our results support the view that covalent bonding is a quantum dynamical phenomenon requiring a properly quantized kinetic energy to be used in its description.

J. Phys. Chem. A 2017, 121, 9330

Covalent bonds are created by the drive of electron waves to lower their kinetic energy through expansion

Michael W. Schmidt,[1] Joseph Ivanic,[2] and Klaus Ruedenberg[1,a)]
[1]*Department of Chemistry and Ames Laboratory USDOE, Iowa State University, Ames, Iowa 50011, USA*
[2]*Advanced Biomedical Computing Center, Information Systems Program, Leidos Biomedical Research, Inc., Frederick National Laboratory for Cancer Research, Frederick, Maryland 21702, USA*

(Received 15 February 2014; accepted 29 April 2014; published online 23 May 2014)

An analysis based on the variation principle shows that in the molecules H_2^+, H_2, B_2, C_2, N_2, O_2, F_2, covalent bonding is driven by the attenuation of the kinetic energy that results from the delocalization of the electronic wave function. For molecular geometries around the equilibrium distance, *two* features of the wave function contribute to this delocalization: (i) Superposition of atomic orbitals extends the electronic wave function from one atom to two or more atoms; (ii) intra-atomic contraction of the atomic orbitals further increases the inter-atomic delocalization. The *inter*-atomic kinetic energy lowering that (perhaps counter-intuitively) is a consequence of the *intra*-atomic contractions *drives* these contractions (which *per se* would increase the energy). Since the contractions necessarily encompass both, the intra-atomic kinetic and potential energy changes (which add to a positive total), the fact that the intra-atomic potential energy change renders the total potential binding energy negative does not alter the fact that it is the kinetic delocalization energy that drives the bond formation. © *2014 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4875735]

J. Chem. Phys. 140, 204104 (2014)